Conductivity Measurements on Pure Ice *

By F. Heinmets and R. Blum

Pioneering Research Division, Quartermaster Research and Engineering Centre,
U.S. Army, Natick, Massachusetts

Conductivity measurements in conditions where all precautions are taken to minimize the experimental errors yield an activation energy of 24·2 kcal for proton transfer in pure ice. There appears to be no measurable threshold potential for proton transfer.

A number of measurements have been made on d.c. conductivity of pure ice.[1-4] Eigen and De Maeyer [5] have pointed out the difficulties and possible sources of errors which may occur in such measurements. There is disagreement about activation energy values and the absolute values appear to be too low (12·3-19·6 kcal). Haas and Hornig [6] have concluded on the basis of spectroscopic studies that the energy for proton transfer in ice is between 27·5 and 18 kcal. This value is much higher than the results from the conductivity measurements.

Since the activation energy is an important parameter for theoretical analysis of proton transport mechanism in ice, an attempt should be made to measure d.c. conductivity temperature dependence more accurately. It was thought possible to carry out more accurate measurements than previously, and simultaneously to take precautions to avoid other sources of errors, such as electrode polarization effects or temperature regulation. The following factors were considered important in such measurements: (*a*) Current values used should be very low and should be recorded directly. (*b*) Polarization at the electrodes should be avoided. In previous d.c. conductivity measurements, metallic electrodes [5] were used. These can be a source of trouble. We introduced a new arrangement where polarization of electrodes was avoided by placing electrodes in liquid phase. (*c*) Special care was taken in purifying water and removing air from the water before freezing it.

Furthermore, the magnitude of the threshold potentials required to carry d.c. currents through the ice may be important in elucidating the d.c. conductivity mechanism in ice. Gränicher *et al.*[4] have stated : " With tensions below 1 V, which is the dissociation potential of water, practically no current is observed." Since we had a favourable measurement arrangement for threshold potentials, it was decided to study this problem carefully.

EXPERIMENTAL

PREPARATION OF WATER AND PURE ICE

The distilled water was redistilled in a special distillation apparatus (designed for production of dust-free water for light scattering measurements). Then the water was passed through a mixed-bed ion-exchange column (Illcoway Research Model De-ionizer) and through a thoroughly flushed millipore filter. Water, thus prepared, could be supercooled to −20°,

---

* On the basis of d.c. conductivity measurements, an activation energy of 20 kcal for pure ice has been reported by Siksna, *Colloqium on the Physics of Ice Crystals* (Erlenbach, Switzerland, 1962).

which indicates high purity. The water was transferred to the conductivity cell (fig. 1); the cell was closed with stopcocks and attached to the vacuum system. In order to remove gases from the water, it was frozen and melted 10 t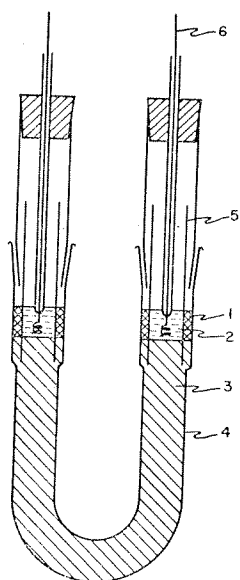imes under vacuum. Subsequently, the bottom of the cell was brought into contact with dry ice, and when a thin ice layer was formed on the cell wall it was transferred to the constant temperature bath. Ice was grown at $-2°$ by lowering the cell into the coolant at a speed of 0·27 cm/h. The ice was clear and flawless and it was maintained at $-2°$ for 23 days before measurements were started. Then the cell was opened and a layer of electrode solution, containing glycerin in 0·01 M HCl, was poured on top of the ice. An electrode solution was prepared for each selected temperature by increasing the glycerin content and storing the solution in the same bath. Its freezing point was adjusted so that it was at temperature equilibrium with the ice. Such solutions were kept in contact with ice for long periods and telescopic inspection and accurate dimensional measurements through both windows showed that the ice surface level was not altered by the solution.

Subsequently platinum electrodes were placed in the electrode solutions and silicone oil was poured between the plastic tube and cell wall (fig. 1). The purpose of the oil was to fill in the space between the ice and cell wall, since the ice separated from the wall when the temperature was lowered. The resistance between bath coolant and electrodes of the cell was extremely high.

FIG. 1.—Conductivity cell. 1, silicone oil; 2, glycerin in 0·01 M HCl; 3, ice; 4, glass cell; 5, plastic (cellulose acetate) tube; 6, platinum electrode.

INSTRUMENTATION AND EQUIPMENT

The temperature bath was of the Dewar-flask type, cooled by circulating flow and equipped with transparent windows. During the measurements, the appearance of the ice was continuously checked by a telescope. The temperature was regulated by a thermistor temperature regulator with an accuracy of $±0·02$ %.

Currents were measured with a Hewlett-Packard d.c. micro-voltammeter (model 425A; range: $10\mu\mu$ A to 3 mA). All wiring was shielded and connections were made as short as possible. A recorder (Varian model G 22) was attached to the ammeter and the current recorded as a function of time.

The accuracy for d.c. measurements was: (i) potential: 1/4 %; (ii) current: 1 % of recorded scale; (iii) temperature: $±0·01°$.

RESULTS

Since electrode polarization is a source of error in d.c. conductivity measurements, a series of studies on such phenomenon by using various electrodes was made. Our experience shows that the polarization effect depends on various experimental factors. With metallic electrodes, it is always present when the current density is high or the temperature low.

Fig. 2 shows current-time relationship with various electrodes. As a control, an ohmic resistance (10^{10} ohms) was recorded. It exhibits an initial switching-transient, but otherwise the resistance is constant. This measurement indicates that the instrumental system is capable of recording high resistance values. At $-20°$, at indicated current range, all three electrodes (fig. 2) can be used for conductivity measurement. It should be noted that ice does not act as an ohmic resistance, since it takes about 10 sec before a constant current value is established. Similarly, after the potential is disconnected, the current is not immediately reduced to zero value.

Fig. 3 shows the effect of a prolonged current at $-20°$. It is evident that the Hg electrode system is polarized, while the Pt/ice holds the current constant. However, when the temperature is lowered to $-30.8°$, the Pt/ice electrode also exhibits polarization effect while the Pt/solution/ice system is unaffected. While platinum electrodes
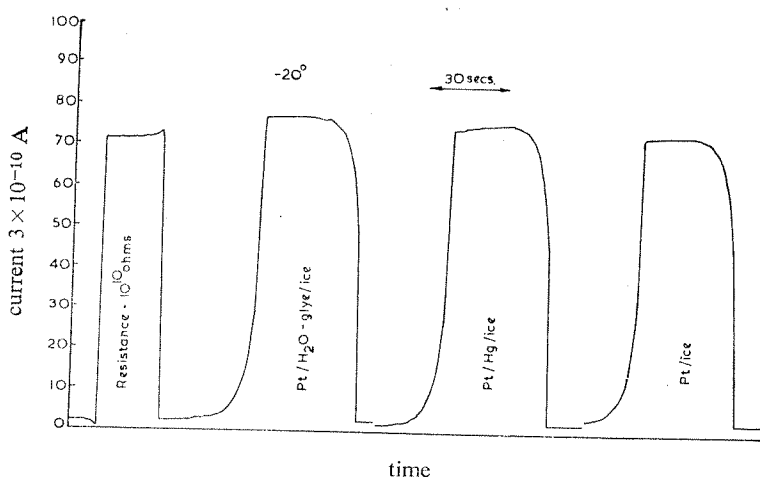

FIG. 2.—Initial current characteristics with various electrode systems at $-20°$. The platinum (black) electrode (Pt/ice) was frozen into distilled water.
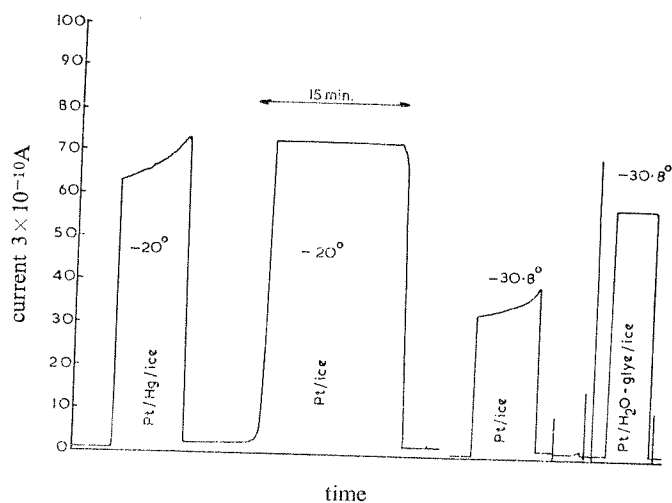

FIG. 3.—Current characteristics as a function of time with various electrode systems at -20 and $-30.8°$.

can be used, since polarization is reduced when frozen into acid solutions, they introduce a source of error when used for a long time. This is because the liberation of gas at the ice/Pt interphase and its accumulation may interfere with solid physical contact. On the basis of all experimental evidence, the Pt/solution/ice electrode system was considered to be the most reliable and was selected for the d.c. conductivity measurements of pure ice.

DETERMINATION OF THRESHOLD POTENTIAL FOR D.C. CONDUCTIVITY OF PURE ICE

In order to measure the threshold potentials, the potential applied to the electrodes was varied over a wide range. Since the current also varied widely, then in order to avoid errors by polarization of electrodes, only the initial stable current values were measured. Pt/Hg/ice and Pt/solution/ice electrode systems yielded similar results except that at higher current values the former was subject to polarization.

Since we used very low potential values, it was essential that the effect of contact and interphase potentials be eliminated. For this purpose, all current measurements were made at two polarities ($\pm$, $\mp$) and only the average current values were used for the determination of conductivities. At low applied potentials, the current values at different polarities were highly dissimilar. However, average values were very consistent.

Data in table 1 show that conductivity of pure ice is practically independent of applied potentials. At small potential values currents become extremely low and there is less accuracy in measurements. At high current values there is a reduction of conductivity.

TABLE 1.—CONDUCTIVITY THRESHOLD MEASUREMENTS FOR PURE ICE AND WATER

pure ice expt. I $-2 \cdot 0°$		pure ice expt. II $-10°$		pure water expt. III $+20°$	
appl. voltage, V	cond. $\times 10^{-9}$ mho	appl. voltage, V	cond. $\times 10^{-9}$ mho	appl. voltage, V	cond. $\times 10^{-5}$ mho
·010	(2·30)	·50	·81	·015	2·37
·020	3·77	1·0	·81	·020	2·40
·050	3·35	1·5	·82	·040	2·50
·100	3·13	12·0	·76	·100	2·45
·500	3·16	94·8	·71	1·00	2·50
1·50	3·16			3·00	2·43
4·40	3·32			4·40	2·40
22·80	3·19				
94·50	(2·97)				

current range:
0·03 to 290 mμ A

current range:
0·03 to 69 mμ A

current range:
0·04 to 100 μ A

Conductivity measurements were carried out with the following electrode systems:
(1) expt. I and II: Hg/ice/Hg; (2) expt. III: Pt (black)/water/Pt.

The conductivity of pure water is similarly constant at a wide range of applied potentials. One may conclude that there is no potential threshold at 20 mV electrode potential in ice and water systems.

D.C. CONDUCTIVITY

Before final measurements, various preliminary studies were made. We observed (as others have) that when the temperature was lowered too rapidly, cracks appeared in the ice. This can be avoided when the temperature is lowered very slowly. Preliminary measurements yielded activation energy (AE) values of 15-19 kcal. However, in all these cases, we had reason to assume that impurities or electrical leaks were involved. Final experiments reported here were carried out under conditions where all known sources of error were removed.

Fig. 4 shows a plot of log conductivity as a function of $1/T$. The activation energy, estimated from a straight slope, is 24·2 kcal. The absolute conductivity is approximately * $1·6 \times 10^{-9}$ mho cm^{-1} at $-10°$.

In another experiment, using a small straight tube as a cell (int. diam. 7·6 mm) containing a short section of ice, an activation energy of 24·3 kcal was obtained. These are the two highest values and we consider these two experiments to be most reliable.
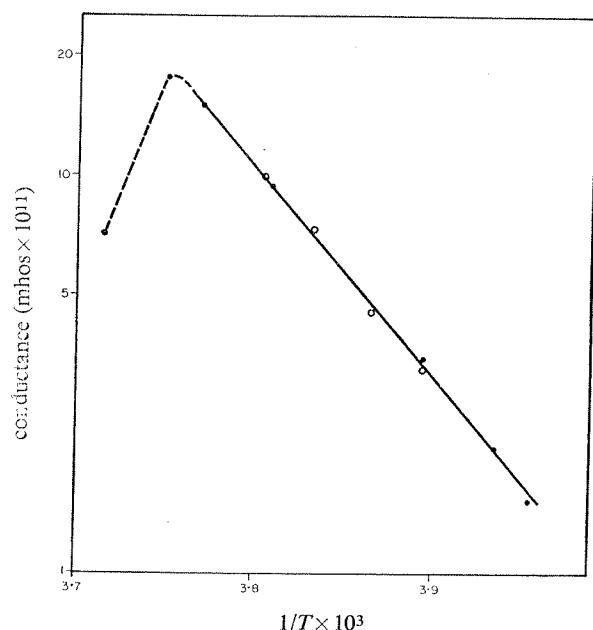

FIG. 4.—Log-conductance of pure ice as a function of $1/T$. Measurements were made during three successive days. Starting at $-2°$, 4 solid circles, 4 open circles and again 3 solid circles indicate the sequence of the measured temperatures.

The conductivity curve has a maximum peak value. This has not previously been reported in ice measurements, although it is a well-known phenomenon in the semi-conductor field.[8] At first, this unexpected peak was considered doubtful. However, it has been observed in many experiments, but only where impurities were greatly reduced. An attempt was made to record the conductivities when the temperature was reversed (from -30 to $-2°$). However, the process is extermely time-consuming, since stable conductivity values are not obtained in a reasonable length of time. Conductivity values measured at intervals of a few hours followed a very irregular pattern. However, when the temperature was again lowered, the maximum conductivity appeared in the same region as during the first experiment.

DISCUSSION

Careful conductivity experiments with pure ice yielded an activation energy of 24·2 kcal. This value is much higher than any determined in many previous studies.[5] However, it is close to the spectrometrically-determined average value, 22·8 kcal.[6] In our experiments, we minimized all possible sources of error and it appears that the highest activation energies are obtained only in conditions of highest purity. The

* cell constant calculated from dimensional measurements.

evidence that only pure ice samples reveal a maximum peak of log-conductivity supports the conclusion that lower activation energies are associated with higher impurity content.[5]   The meaning of the reduction of conductivity (at $-7°$) is not clear.   In the semiconductor field, this phenomenon is interpreted as indicating that carrier concentration reaches a maximum while the mobility of the carriers decreases with rising temperature due to " lattice scattering ".[7]   Since this phenomenon is not observed with doped ice, where proton-hole transfer mechanism is dominant, it appears that the rotational properties of the proton-transferring system may be involved in this phenomenon.[8, 9]

Our experiments suggest that there is no definite threshold potential in proton transfer in ice.   This can be demonstrated only at very small current values.   Otherwise, polarization and electrolysis effects " mask " the phenomenon.

[1] Johnstone, *J. Amer. Chem. Soc.*, 1909, **31**, 1025.
[2] Johnstone, *Proc. Trans. Nova Scotian Inst. Sci.*, 1912, **13**, 126
[3] Bradley, *Trans, Faraday Soc.*, 1957, **53**, 687.
[4] Gränicher, Jacard, Scherrer and Steinemann, *Disc. Faraday Soc.*, 1957, **23**, 50.
[5] Eigen and De Maeyer, *Proc. Roy. Soc. A*, 1958, **247**, 505.
[6] Haas and Hornig, *J. Chem. Physics*, 1960, **32**, 1763.
[7] Hannay, in *Semiconductors* (Reinhold Publishing Corp., New York, 1959), p. 1.
[8] Steinemann and Gränicher, *Helv. physic. Acta*, 1957, **30**, 553.
[9] Steinemann, *Helv. physic. Acta*, 1957, **30**, 581.